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OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY

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CRYSTAL AND MOLECULAR STRUCTURE OF  $(CH_3)_2SN(C_6H_5CR(CO)_3)_2 \cdot (U)$

MAY 81 U SCHUBERT, B R WILLEFORD

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contains molecules of both configurations in equal numbers. The geometry of the four groups around the tin atom is approximately tetrahedral; thus, anomalous spectral properties of this compound cannot be attributed to molecular distortions of the normal tin geometry.

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Crystal and Molecular Structure of  $(\text{CH}_3)_2\text{Sn}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2$

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Summary

$\eta^6, \eta^6$ -Dimethyldiphenylstannane-bis-tricarbonylchromium,  $(\text{CH}_3)_2\text{Sn}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2$ , crystallizes in the orthorhombic space group  $\text{Pna}2_1$  with  $Z = 4$ ,  $a = 2663(2)$ ,  $b = 1032.0(8)$ ,  $c = 762.7(3)$  pm,  $V = 2096 \times 10^6 \text{ pm}^3$ . The crystal structure has been determined by the heavy atom method and refined to final  $R$  values of  $R = 0.055$  and  $R_w = 0.059$  for 1789 independent reflections using  $\text{Mo-K}_\alpha$  radiation. In the lattice, the molecule is disordered in that one of the  $\text{Cr}(\text{CO})_3$  groups can be on either side of the phenyl ring to which it is bonded; the unit cell contains molecules of both configurations in equal numbers. The geometry of the four groups around the tin atom is approximately tetrahedral; thus, anomalous spectral properties of this compound cannot be attributed to molecular distortions of the normal tin geometry.

Introduction

Several years ago, Willeford, Zuckerman and coworkers reported the results of a spectroscopic investigation of several arene metal carbonyl complexes of tin-containing ligands [2]. All but one of the complexes studied showed tin-methyl stretching absorptions in the infrared practically identical with those of the uncomplexed ligands. That one exception was  $\eta^6, \eta^6$ -dimethyldiphenylstannane-bis-tricarbonylchromium,  $(\text{CH}_3)_2\text{Sn}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2$ . This complex showed no absorption in the infrared region where the symmetric tin-methyl stretching

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vibration would be expected to occur. Raman spectroscopy revealed a strong polarized band coincident with the infrared absorption assigned to the asymmetric tin-methyl vibration. Thus, the symmetric and asymmetric tin-methyl vibrations in this complex apparently are degenerate. Gross distortion of the tin atom in this complex from its usual tetrahedral symmetry was suggested as a possible explanation for this unusual observation. A crystallographic investigation was undertaken to determine the validity of this conjecture.

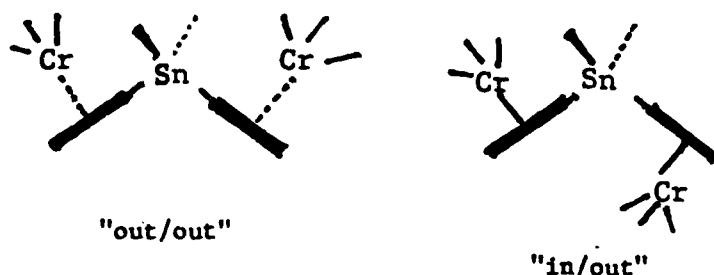
### Experimental

First attempts to grow single crystals of the complex resulted only in twinned crystals. Satisfactory crystals were finally obtained by careful layering of oxygen-free hexane over a concentrated solution of the complex in benzene. After several days standing at ambient temperature, crystals formed at the benzene-hexane interface which were collected, washed with hexane, and dried under vacuum. A crystal, approximately 0.4 x 0.4 x 0.8 mm. was mounted on a Syntex P2<sub>1</sub> four circle automatic diffractometer. Lattice parameters (see Table 1) were determined by least squares from the setting angles of 15 reflections from different parts of the reciprocal space. Mo-K $\alpha$  radiation was used (graphite monochromator,  $\lambda = 71.069$  pm) for intensity data collection ( $\omega$ -scan,  $\Delta\omega = 0.9^\circ$ , 1789 independent reflections,  $2^\circ \leq 2\theta \leq 46^\circ$ ). The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by the heavy atom method and refined by full matrix least squares. Only the metal atoms were treated anisotropically. The hydrogen atom parameters were kept constant during refinement. For 1573 structure factors with  $F_o \geq 3.92 \sigma(F_o)$  final  $R = 0.055$  and  $R_w = 0.059$  were obtained ( $1/w = \sigma^2(F_o)$ ).

Table 2 shows the final atomic parameters, while Table 3 gives intramolecular distances and angles.

#### Description of the structure and discussion

For this compound two favorable isomers can be imagined:



For steric reasons, "in/in" complexes are formed only if there is a metal-metal bond [as in  $\text{Fe}_2(\text{CO})_4(\pi\text{-C}_5\text{H}_5\text{-SiMe}_2\text{-}\pi\text{-C}_5\text{H}_5)$  [3]]. Rotation of the phenyl rings about the  $\text{Sn-C}_{\text{phenyl}}$  axes is hindered by interactions between the phenyl rings and is not to be expected.

Because of the disorder of one of the  $\text{Cr}(\text{CO})_3$  moieties, both "out/out" and "in/out" isomers are present in the crystal. The figure shows the superposition of both isomers. Whereas the positions of the  $\text{Ph}_2\text{SnMe}_2$  moiety and one of the  $\text{Cr}(\text{CO})_3$  groups [the one which is "out" in both isomers, Cr(1)] are not affected by the disorder, the positions of Cr(2) and Cr(3) are only half-occupied. The CO ligands of the disordered  $\text{Cr}(\text{CO})_3$  moiety are positioned in such a way that two oxygen atoms [O(4) and O(5)] and one carbon atom [C(6)] on Cr(2) have common coordinates with the analogous atoms at Cr(3) of the neighboring molecule  $(0.5-x, -0.5+y, 0.5+z)$ .

Because of the disorder in the crystal, the  $\text{Cr-C}_{\text{CO}}$  and  $\text{Cr-C}_{\text{ph}}$  distances and the  $\text{Cr-C-O}$  angles are found to differ considerably and have large standard deviations (see Table 3). However, their mean values are quite similar. The

CO ligands and the carbons of the phenyl groups are staggered. The phenyl rings are planar within 1.8 standard deviations. Whereas Cr(1) is located above the center of the phenyl ring, the distances of Cr(2) and Cr(3) to C(21) and C(22) are somewhat longer than to C(24) and C(25) (see Table 3). The Cr-phenyl plane distances are 170.1 (Cr 1), 162.6 (Cr 2) and 163.8 (Cr 3) pm respectively. Because of the disorder, a more detailed discussion of the bond lengths and angles is not justified.

The tin atom is located 8 and 9 pm outside the best planes of the phenyl rings (towards the "out" position). Its coordination is approximately tetrahedral. The Sn-C<sub>phenyl</sub> bond lengths (218 pm) are slightly longer than in tetraphenyltin [4] or in triphenyltin compounds [5-8], where bond lengths of 212-216 pm are found.

The results give a dimethyltin carbon-tin-carbon angle of  $115.5(7)^\circ$ , opened from the tetrahedral value at the expense of the diphenyltin angle of  $105.7(5)^\circ$  which is somewhat closed. Structural data on the free dimethyldiphenylstannane ligand, or on any simple, mixed methylphenyltin system are lacking [8]. Apparently there are structural data for only two compounds in which both unsubstituted methyl and phenyl groups are attached to the same tin atom [9] (the structures of  $\text{Ph}_3\text{SnCH}_2\text{I}$  [10] and a ring system based upon 1,8-bis-dimethylstannyl naphthalene [11] do not offer meaningful comparison). These compounds, 4-chloro- and 4-bromo-1,2,3,4-tetraphenylbutadienyldimethylphenylstannane, exhibit closed dimethyltin carbon-tin-carbon angles of  $105.5^\circ$  and  $104.5^\circ$ , respectively, while the mean methylphenyltin angles are  $107.7^\circ$  and  $108.4^\circ$ , respectively. The bonds involving the vinylic system are opened to even larger angles [9]. This is opposite to what is observed in the title compound, where the relative magnitudes of the dimethyltin and diphenyltin angles (the methylphenyltin angles are intermediate in value) reflect a greater concentration of s-character in the bonds the tin atom exerts to hold the methyl groups, and a greater concentration of p-character toward the phenyl groups. Thus the phenyl groups in this case are exhibiting a greater electronegativity.

The direction of the relative opening of the dimethyltin angles is in accord with the suggestion of Willeford and Zuckerman [1], but a distortion of this small magnitude ( $6.0^\circ$  from tetrahedral,  $64.5^\circ$  from linear), while of interest, obviously cannot lie at the root of the absence of the symmetric Sn-C stretching absorption in the infrared spectrum and the presence in the Raman spectrum of only a single absorption in this region. Other rationalizations of these spectroscopic data must be sought.

#### Acknowledgments

We thank Prof. Dr. E. O. Fischer for his interest and for making available the facilities of the Institute. B.R.W. thanks the Deutscher Akademischer Austauschdienst, Bonn, for financial support and the Fulbright Kommission, Bonn, for a travel grant.

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Figure Caption

A perspective drawing of the molecular structure of  $\eta^6, \eta^6$ -dimethyldiphenylstannane-bis-tricarbonylchromium,  $(CH_3)_2Sn[C_6H_5Cr(CO)_3]_2$ . The disordered part of the molecule is drawn with light dotted lines. The hydrogen atoms are omitted for clarity.

Table 1

Crystal Data

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Formula (molecular weight)	$C_{20}H_{16}Cr_2O_6Sn$ (575.0)
Space group	$Pna2_1$ ( $Z = 4$ )
Cell constants: $a, b, c$	2663(2), 1032.0(8), 762.7(3) [pm]
$V$	$2096 \cdot 10^6$ [pm <sup>3</sup> ]
Density (calc.)	1.82 [g/cm <sup>3</sup> ]
Linear absorption coeff. (Mo-K $_{\alpha}$ )	22.8 [cm <sup>-1</sup> ]

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Table 2: atomic parameters

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Sn	0.13242(3)	0.01223(8)	0.1		Cr3	0.2600(2)	-0.1047(4)	0.3246(6)	
Cr1	0.03568(7)	-0.2736(2)	0.1423(4)		Cr2	0.2634(2)	0.1526(4)	0.0753(8)	
Co1	0.1011(7)	0.095(2)	0.337(3)	4.8(4)	Co2	0.1156(7)	0.116(2)	-0.140(3)	4.7(4)
Cr10	0.1087(5)	-0.187(1)	0.072(2)	3.0(3)	Cr20	0.2175(4)	0.005(1)	0.139(2)	2.9(3)
Cr11	0.0844(6)	-0.230(2)	-0.087(2)	4.2(3)	Cr21	0.2346(7)	0.069(2)	0.281(3)	5.5(4)
Cr12	0.0665(7)	-0.359(2)	-0.095(3)	5.2(4)	Cr22	0.2889(7)	0.074(2)	0.299(3)	5.5(4)
Cr13	0.0753(7)	-0.445(2)	0.042(2)	4.5(4)	Cr23	0.3165(6)	0.006(2)	0.189(2)	3.8(3)
Cr14	0.0988(7)	-0.408(2)	0.184(3)	5.3(4)	Cr24	0.2963(6)	-0.062(2)	0.053(2)	4.2(4)
Cr15	0.1164(6)	-0.276(1)	0.201(2)	3.9(3)	Cr25	0.2445(6)	-0.062(2)	0.028(2)	3.8(3)
Cr1	0.0200(7)	-0.281(2)	0.368(3)	4.7(4)	O4	0.1765(4)	0.342(1)	0.120(2)	5.9(3)
O1	0.0081(5)	-0.287(1)	0.514(2)	7.3(4)	Cr41	0.218(1)	0.278(3)	0.103(6)	5.0(7)
Cr2	-0.0255(5)	-0.345(1)	0.094(3)	3.9(3)	Cr42	0.1970(9)	0.361(2)	0.005(4)	1.8(4)
O2	-0.0647(4)	-0.389(1)	0.062(2)	5.1(3)	O5	0.3275(5)	0.372(1)	0.095(3)	7.6(3)
Cr3	0.0068(5)	-0.114(1)	0.123(3)	3.9(3)	Cr51	0.307(1)	0.282(3)	0.092(6)	4.5(6)
O3	-0.0097(4)	-0.010(1)	0.127(2)	4.8(2)	Cr52	0.287(1)	0.382(3)	-0.014(4)	2.9(6)
H11	0.081	-0.174	-0.187	5.0	Cr6	0.255(1)	0.195(3)	-0.191(5)	9.3(8)
H12	0.047	-0.387	-0.194	5.0	Cr61	0.2513(9)	0.111(3)	-0.266(4)	5.2(6)
H13	0.054	-0.533	0.029	5.0	Cr62	0.251(1)	0.195(3)	-0.312(5)	7.3(8)
H14	0.104	-0.471	0.277	5.0	H23	0.353	0.006	0.208	5.0
H15	0.135	-0.252	0.306	5.0	H24	0.319	-0.104	-0.028	5.0
H21	0.213	0.115	0.304	5.0	H25	0.230	-0.108	-0.008	5.0

table 2 continued

atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Sn	2.24(3)	3.64(4)	4.18(4)	-0.17(3)	0.03(6)	-0.11(7)
Cr1	2.24(8)	2.76(9)	3.94(13)	-0.21(7)	-0.15(9)	0.13(10)
Cr2	2.7(2)	3.4(2)	3.5(3)	-0.3(2)	-0.1(2)	0.0(2)
Cr3	1.6(2)	2.1(2)	2.2(2)	0.1(1)	-0.2(2)	-0.1(2)

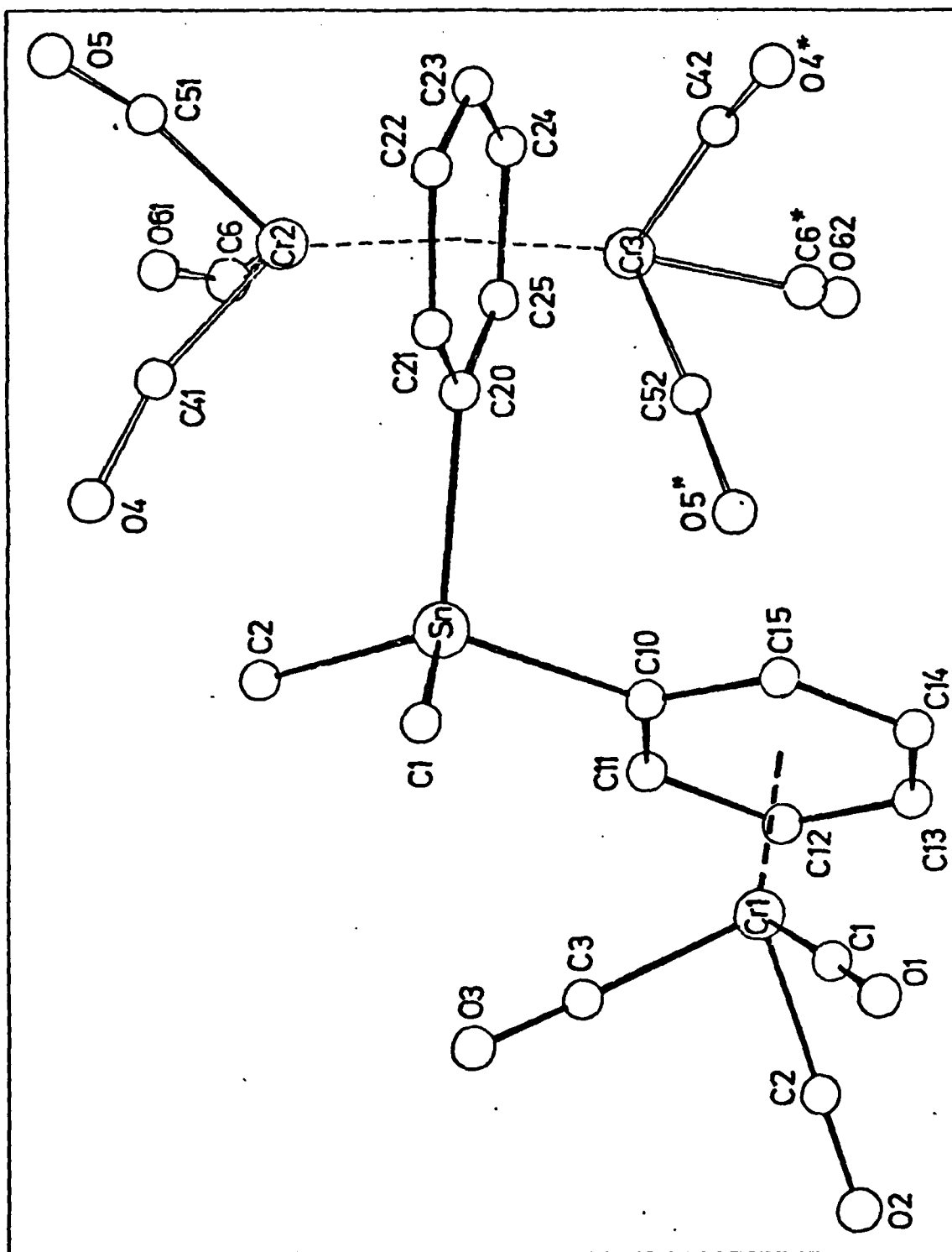
The anisotropic thermal parameter is defined:

$$T = \exp[-1/4(h^2 a^2 B_{11} + k^2 b^2 B_{22} + l^2 c^2 B_{33} + 2hka \cdot b \cdot B_{12} + 2hla \cdot c \cdot B_{13} + 2klb \cdot c \cdot B_{23})]. B_{ij} \text{ in } 10^4 \text{ pm}^2.$$

Table 3: Distances (in pm) and angles (in °):

Sn-C01	216(2)		Sn-C02	217(2)	
Sn-C10	218(1)		Sn-C20	218(1)	
Cr1-C1	177(2)	mean: 181	Cr1-C10	221(1)	mean: 220
Cr1-C2	182(1)		Cr1-C11	222(2)	
Cr1-C3	183(1)		Cr1-C12	217(2)	
C1-O1	116(3)		Cr1-C13	219(2)	
C2-O2	117(2)		Cr1-C14	220(2)	
C3-O3	116(2)		Cr1-C15	220(2)	
Cr2-C41	179(3)	mean: 189	Cr2-C20	208(1)	mean: 216
Cr2-C51	178(3)		Cr2-C21	195(2)	
Cr2-C6	210(4)		Cr2-C22	201(2)	
C41-O4	129(3)		Cr2-C23	225(2)	
C51-O5	107(3)		Cr2-C24	239(2)	
C6-O62	92(5)		Cr2-C25	230(2)	
Cr3-C42	183(3)	mean: 190	Cr3-C20	220(1)	mean: 216
Cr3-C52	177(3)		Cr3-C21	195(2)	
Cr3-C6*	210(3)		Cr3-C22	201(2)	
C42-O4*	105(3)		Cr3-C23	216(2)	
C52-O5*	136(3)		Cr3-C24	233(2)	
C6-O61	105(4)		Cr3-C25	234(2)	
C01-Sn-C02	115.5(7)		C1-Cr1-C2	88.2(8)	
C01-Sn-C10	110.2(6)		C1-Cr1-C3	91.1(8)	
C01-Sn-C20	106.4(6)		C2-Cr1-C3	88.3(8)	
C02-Sn-C10	109.0(6)		C41-Cr2-C51	84.1(16)	
C02-Sn-C20	109.7(6)		C41-Cr2-C6	83.5(15)	
C10-Sn-C20	105.7(5)		C51-Cr2-C6	89.2(14)	
			C42-Cr3-C52	84.7(12)	
			C6-Cr3-C52	80.4(13)	
			C6-Cr3-C42	88.2(12)	

\* 0.5-x, -0.5+y, 0.5+z



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